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<p>(21) International Application Number: PCT/CA96/00773</p> <p>(22) International Filing Date: 25 November 1996 (25.11.96)</p> <p>(30) Priority Data: 08/574,262 18 December 1995 (18.12.95) US</p> <p>(71) Applicant (for all designated States except US): BALLARD POWER SYSTEMS INC. [CA/CA]; 9000 Glenlyon Parkway, Burnaby, British Columbia V5J 5J9 (CA).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): WILKINSON, David, P. [CA/CA]; 1391 Coleman Street, North Vancouver, British Columbia V7R 1W4 (CA). JOHNSON, Mark, C. [US/US]; 4702 N. 33rd Place, Phoenix, AZ 85018 (US). COLBOW, Kevin, M. [CA/CA]; 1305 Fernwood Crescent, North Vancouver, British Columbia V7P 1K3 (CA). CAMPBELL, Stephen, A. [GB/CA]; 725 Delestre Avenue, Coquitlam, British Columbia V3K 2G2 (CA).</p> <p>(74) Agent: RUSSELL REYNEKE; Two Bentall Centre, Suite 700, 555 Burrard Street, Vancouver, British Columbia V7X 1M8 (CA).</p>		<p>(81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> With international search report.</p>
<p>(54) Title: METHOD AND APPARATUS FOR REDUCING REACTANT CROSSOVER IN AN ELECTROCHEMICAL FUEL CELL</p>		
<p>(57) Abstract</p> <p>In an electrochemical fuel cell, a sufficient quantity of catalyst, effective for promoting the reaction of reactant supplied to an electrode, is disposed within the volume of the electrode so that a reactant introduced at a first major surface of the electrode is substantially completely reacted upon contacting the second major surface. Crossover of reactant from one electrode to the other electrode through the electrolyte in an electrochemical fuel cell is thereby reduced.</p> <div data-bbox="763 1176 1347 1785"> </div>		

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METHOD AND APPARATUS FOR REDUCING REACTANT  
CROSSOVER IN AN ELECTROCHEMICAL FUEL CELL

Field Of The Invention

The invention relates generally to electrochemical fuel cells and, more particularly, to a fuel cell with an electrode having catalyst  
5 disposed within the volume between its major surfaces. A method and apparatus for reducing reactant crossover from one electrode to the other in an electrochemical fuel cell is provided.

Background Of The Invention

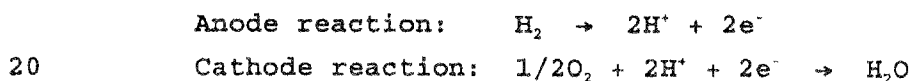
10 Electrochemical fuel cells convert fuel and oxidant to electricity and reaction product. Fluid reactants are supplied to a pair of electrodes which are in contact with and separated by an electrolyte. The electrolyte may be a solid or a  
15 liquid (supported liquid matrix). Solid polymer electrochemical fuel cells generally employ a membrane electrode assembly comprising a solid ionomer or ion-exchange membrane disposed between two planar electrodes. The electrodes typically  
20 comprise an electrode substrate and an electrocatalyst layer disposed upon one major surface of the electrode substrate. The electrode substrate typically comprises a sheet of porous, electrically conductive material, such as carbon  
25 fiber paper or carbon cloth. The layer of electrocatalyst is typically in the form of finely comminuted metal, typically platinum, and is disposed on the surface of the electrode substrate

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at the interface with the membrane electrolyte in order to induce the desired electrochemical reaction. In a single cell, the electrodes are electrically coupled to provide a path for  
5 conducting electrons between the electrodes through an external load.

At the anode, the fuel moves through the porous anode substrate and is oxidized at the anode electrocatalyst layer. At the cathode, the oxidant  
10 moves through the porous cathode substrate and is reduced at the cathode electrocatalyst layer.

Electrochemical fuel cells most commonly employ gaseous fuels and oxidants, for example, those operating on molecular hydrogen as the fuel  
15 and oxygen in air or a carrier gas (or substantially pure oxygen) as the oxidant. The anode and cathode reactions in hydrogen/oxygen fuel cells are shown in the following equations:



The catalyzed reaction at the anode produces hydrogen cations (protons) from the fuel supply. The ion-exchange membrane facilitates the migration of protons from the anode to the cathode. In  
25 addition to conducting protons, the membrane isolates the hydrogen-containing gaseous fuel stream from the oxygen-containing gaseous oxidant stream. At the cathode electrocatalyst layer, oxygen reacts with the protons that have crossed  
30 the membrane to form water as the reaction product.

In liquid feed electrochemical fuel cells, one or more of the reactants is introduced to the

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electrocatalyst in the liquid form. Examples of electrochemical fuel cells which can be operated with a liquid fuel feed are those employing a lower alcohol, most commonly methanol, as the fuel

5 supplied to the anode (so-called "direct methanol" fuel cells) and oxygen to the cathode. In fuel cells of this type the reaction at the anode produces protons, as in the hydrogen/oxygen fuel cell described above, however the protons (along

10 with carbon dioxide) arise from the oxidation of methanol. An electrocatalyst promotes the methanol oxidation at the anode. The methanol may alternatively be supplied to the anode as vapor, but it is generally advantageous to supply the

15 methanol to the anode as a liquid, preferably as an aqueous solution. In some situations, an acidic aqueous methanol solution is the preferred feed to the anode. The anode and cathode reactions in a direct methanol fuel cell are shown in the

20 following equations:

Anode reaction:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + \text{CO}_2 + 6\text{e}^-$

Cathode reaction:  $3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$

Overall reaction:  $\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

The protons formed at the anode

25 electrocatalyst migrate through the ion-exchange membrane from the anode to the cathode, and at the cathode electrocatalyst layer, the oxidant reacts with the protons to form water.

Other non-alcohol fuels may be used in liquid

30 feed fuel cells, for example formic acid. The oxidant may also be supplied as a liquid, for

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example, as an organic fluid with a high oxygen concentration (see U.S. Patent No. 5,185,218), or as a hydrogen peroxide solution.

5 In electrochemical fuel cells employing liquid or solid electrolytes and gaseous or liquid reactant streams, crossover of a reactant from one electrode to the other is generally undesirable. Reactant crossover may occur if the electrolyte is permeable to the reactant, that is, some of a  
10 reactant introduced at a first electrode of the fuel cell may pass through the electrolyte to the second electrode, instead of reacting at the first electrode. Reactant crossover typically causes a decrease in both reactant utilization efficiency and fuel cell performance. Fuel cell performance  
15 is defined as the voltage output from the cell at a given current density or vice versa; the higher the voltage at a given current density or the higher the current density at a given voltage, the better the performance.  
20

In solid polymer electrochemical fuel cells the ion-exchange membrane may be permeable to one or more of the reactants. For example, ion-exchange membranes typically employed in solid  
25 polymer electrochemical fuel cells are permeable to methanol, thus methanol which contacts the membrane prior to participating in the oxidation reaction can cross over to the cathode side. Diffusion of methanol fuel from the anode to the cathode leads  
30 to a reduction in fuel utilization efficiency and to performance losses (see, for example, S. Surampudi et al., Journal of Power Sources, vol.47, 377-385 (1994) and C. Pu et al., Journal of the Electrochemical Society, vol. 142, L119-120

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(1995)).

Fuel utilization efficiency losses arise from methanol diffusion away from the anode because some of the methanol which would otherwise participate in the oxidation reaction at the anode and supply electrons to do work through the external circuit is lost. Methanol arriving at the cathode may be lost through vaporization into the oxidant stream, or may be oxidized at the cathode electrocatalyst, consuming oxidant, as follows:



Methanol diffusion to the cathode may lead to a decrease in fuel cell performance. The oxidation of methanol at the cathode reduces the concentration of oxygen at the electrocatalyst and may affect access of the oxidant to the electrocatalyst (mass transport issues). Further, depending upon the nature of the cathode electrocatalyst and the oxidant supply, the electrocatalyst may be poisoned by methanol oxidation products, or sintered by the methanol oxidation reaction.

The electrode structures presently used in direct methanol solid polymer fuel cells were originally developed for hydrogen/oxygen fuel cells. The anode electrocatalyst which promotes the oxidation of methanol to produce protons is typically provided as a thin layer adjacent to the ion-exchange membrane (see U.S. Patent Nos. 5,132,193 and 5,409,785 and European Patent Publication No. 0090358). The anode electrocatalyst layer is typically applied as a

coating to one major surface of a sheet of porous, electrically conductive sheet material or to one surface of the ion-exchange membrane. This provides a limited reaction zone in which the methanol can be oxidized before contacting the membrane electrolyte. Thus, with this type of electrode, the methanol concentration at the anode-electrolyte interface will typically be high.

Reactant crossover may be substantially eliminated if a reactant introduced to a first major surface of a fuel cell electrode is substantially completely reacted on contacting the second major surface of the electrode. In this case essentially no unreacted reactant would be available to pass from the second surface through the electrolyte to the other electrode. As described herein, this may be accomplished by ensuring that the reactant contacts sufficient catalyst so that it is substantially completely reacted before it contacts the second surface of the electrode.

It is therefore an object of the invention to provide an electrochemical fuel cell in which crossover of a reactant from one electrode to the other is reduced.

It is a further object of the invention to provide a solid polymer electrochemical fuel cell in which a reactant is substantially completely reacted before it contacts the membrane electrolyte.

It is a still further object of the invention to provide a direct methanol solid polymer fuel cell in which methanol crossover from the anode to the cathode is reduced.



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Another object of the invention is to provide a method for reducing reactant crossover in an electrochemical fuel cell.

#### Summary Of The Invention

5           The above and other objects are achieved by an electrochemical fuel cell in which an electrode has catalyst disposed within the volume thereof. The electrochemical fuel cell comprises:

10           (a) a first electrode, the first electrode having first and second oppositely facing major surfaces, the first electrode comprising at least one layer of porous material and a sufficient quantity of catalyst disposed within the volume of  
15           the electrode between the major surfaces so that a reactant in a fluid introduced to the first major surface of the first electrode is substantially completely reacted upon contacting the second major  
20           surface of the first electrode;

          (b) a second electrode;

          (c) an electrolyte interposed between the second major surface of the first electrode and the second electrode.

25           In a preferred aspect of an electrochemical fuel cell the first and second oppositely facing major surfaces of the first electrode are planar.

          In one embodiment the catalyst is distributed substantially uniformly within the volume between  
30           the first and second oppositely facing major surfaces of the first electrode. In an alternative embodiment the catalyst is distributed

nonuniformly, such as, for example, in discrete layers or regions. The at least one layer of porous material may optionally comprise a plurality of stacked layers, and may optionally further  
5 comprise carbon particles. Suitable carbon particles include acetylene blacks, furnace blacks and graphite particles.

The electrolyte may be a liquid or a solid. With a liquid electrolyte a porous, electrically  
10 non-conductive separator is typically employed between the two electrodes. In a preferred embodiment the electrochemical fuel cell is a solid polymer fuel cell and the electrolyte comprises an ion-exchange membrane. The at least one layer of  
15 porous material is preferably electrically conductive and in a further embodiment comprises a proton conductor. Preferred porous materials comprise electrically conductive sheet material such as carbon fiber paper or carbon cloth. In an  
20 alternative aspect the at least one layer of porous material comprises carbon particles and a polymeric binder.

The fluid in which the reactant is introduced may be a liquid or a gas.

25 In a preferred embodiment of a liquid feed electrochemical fuel cell, the first electrode is an anode and the reactant comprises an alcohol, preferably methanol. In this case the catalyst promotes the oxidation of methanol. The fluid in  
30 which the methanol is introduced preferably comprises water and may optionally further comprise acid. In a preferred embodiment of a liquid feed direct methanol fuel cell the at least one layer of porous material comprises a plurality of carbon

fiber paper layers each of the layers having two oppositely facing major surfaces, wherein catalyst is disposed on at least one major surface of each of the layers.

5           In any of the above embodiments of a solid polymer electrochemical fuel cell, catalyst may also be applied to the surface of the ion-exchange membrane.

10           The electrode has first and second oppositely facing major surfaces and comprises:

- (a) at least one layer of porous material;
  - (b) a sufficient quantity of catalyst disposed within the volume of the electrode between the major surfaces so that a reactant in a fluid introduced to the first major surface of the electrode is substantially completely reacted upon contacting the second major surface of the electrode.
- 15

20           In a preferred aspect of an electrode the first and second oppositely facing major surfaces of the electrode are planar.

          In the electrode, the porous material acts as a carrier for the catalyst, and is preferably liquid and gas permeable, to allow gas or liquid feed reactant to penetrate it and to allow gaseous products to escape. The porous material may be electrically non-conductive or preferably electrically conductive. The electrode, as a whole, is electrically conductive, however non-conductive porous material incorporating sufficient catalyst and/or other electrically conductive material to render the electrode electrically conductive may be used. The porous material may,

25

30

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for example, be one or more layers of electrically conductive particles, such as carbon particles, and a polymeric binder. The preferred porous material includes a sheet material which is self-supporting and has structural integrity, thus providing structural support for the adjacent ion-exchange membrane in solid polymer fuel cells. Suitable non-conductive sheet materials include expanded polytetrafluoroethylene and glass fiber matting, which preferably have electrically conductive particles, such as, for example, carbon particles associated therewith. Suitable electrically conductive sheet materials include carbon aerogel, carbon foam, carbon sponge, expanded metals and reticulated metals. Preferred sheet materials include carbon fiber paper and carbon cloth. The electrode may optionally incorporate structures to facilitate movement of gaseous products away from the electrode, for example, channels, grooves and layers or regions of different porosities.

In general, in electrochemical fuel cells, higher catalyst loadings lead to improved performance. The electrode structures described herein facilitate use of higher catalyst loadings.

In a method of substantially completely reacting a reactant in a fluid within a first electrode of an electrochemical fuel cell, the first electrode having first and second oppositely facing major surfaces, the reactant introduced at the first major surface, the first electrode comprising at least one layer of porous material and a catalyst, and the fuel cell further comprising a second electrode and an electrolyte interposed between the second major surface of the

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first electrode and the second electrode, the method comprises:

5 disposing a sufficient quantity of the catalyst within the volume of the first electrode between the major surfaces thereof such that the reactant is substantially completely reacted upon contacting the second major surface.

#### Brief Description Of The Drawings

10 FIG. 1A is an exploded side view of a typical solid polymer electrochemical fuel cell showing a conventional membrane electrode assembly interposed between two separator plates, the separator plates having reactant flow channels formed in the  
15 surfaces for directing the reactants to the electrodes.

FIG. 1B is a side sectional view of a conventional (prior art) solid polymer electrochemical fuel cell electrode having the  
20 catalyst disposed in a single, discrete layer at the interface with the membrane electrolyte.

FIG. 2 is a side sectional view of an electrode having catalyst substantially uniformly distributed throughout the volume of the electrode.

25 FIG. 3 is a side sectional view of an electrode having a catalyst layer impregnated into, and disposed in the volume underlying, the surface of the electrode facing away from the membrane electrolyte.

30 FIG. 4 is a side sectional view of an electrode having a catalyst layer impregnated into both surfaces of the electrode.

FIG. 5 is a side sectional view of an

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electrode comprising two layers of porous electrically conductive material and an active layer comprising catalyst interposed between them.

5 FIG. 6 is a side sectional view of a multi-layer electrode comprising four layers of porous electrically conductive material and catalyst disposed at both surfaces of each layer.

10 FIG. 7 is a side sectional view of a multi-layer electrode comprising five layers of porous electrically conductive material and catalyst disposed within alternate layers.

15 FIG. 8 is a side sectional view of a multi-layer electrode structured to facilitate escape of gaseous products, comprising three layers of porous electrically conductive material.

FIG. 9 is a plot of cell voltage versus methanol utilization for a fuel cell with the conventional anode (plot A) shown in FIG. 1B and with a multi-layer anode (plot B) shown in FIG. 6.

20 Detailed Description Of The Preferred Embodiments

FIG. 1A illustrates a typical solid polymer fuel cell 10. Fuel cell 10 includes a membrane electrode assembly 12 consisting of an ion-exchange membrane 14 interposed between two electrodes, namely an anode 16 and a cathode 17. In 25 conventional solid polymer fuel cells, anode 16 and cathode 17 comprise a substrate of porous electrically conductive sheet material, 18 and 19, respectively. Each substrate has a thin layer, 20, 30 21, of electrocatalyst disposed on one of the major surfaces at the interface with the membrane 14. The membrane electrode assembly 12 is typically interposed between anode flow field or separator

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plate 22 and cathode flow field or separator plate 24. Anode separator plate 22 has at least one fuel flow channel 23 engraved, milled or molded in its surface facing anode. Similarly, cathode separator plate 24 has at least one oxidant flow channel 25 engraved, milled or molded in its surface facing the cathode. When assembled against the co-operating surfaces of electrodes 16 and 17, channels 23 and 25 form the reactant flow field passages for the fuel and oxidant respectively.

FIG. 1B shows a conventional (prior art) electrode 30 of the type typically used in solid polymer fuel cells. Electrode 30 comprises a sheet of porous, electrically conductive material 32, typically carbon fiber paper or carbon cloth. The electrode 30 has oppositely facing major planar surfaces 30a, 30b. In a conventional solid polymer fuel cell, electrode surface 30b is adjacent to the membrane electrolyte. A thin layer comprising electrocatalyst particles 36 is disposed at electrode surface 30b.

FIG. 2 shows an electrode 40 comprising porous material 42. The electrode 40 has oppositely facing major planar surfaces 40a, 40b. In a direct methanol fuel cell, electrode surface 40b is adjacent to the membrane electrolyte. Catalyst particles 46, effective for promoting the oxidation of methanol, are distributed between the electrode surfaces 40a, 40b. The catalyst particles 46 may be distributed substantially uniformly throughout the volume between the electrode surfaces 40a, 40b, as shown in FIG. 2, or may be distributed nonuniformly, for example, in discrete layers or regions. Sufficient catalyst is provided so that

substantially all of the methanol, which is introduced in a fluid to the electrode 40 at surface 40a is oxidized upon contacting surface 40b. The thickness of the electrode 40 and the quantity of catalyst required will depend for example on the rate of methanol supply to the electrode 40, and the rate of fluid transport through the electrode 40. In one example of an electrode 40, porous material 42 is one or more layers of carbon particles mixed with a polymeric binder, and catalyst particles 46 are distributed throughout porous material 42. In another example of an electrode 40, porous material 42 is glass fiber mat or expanded (porous) polytetrafluoroethylene and a matrix of carbon particles and a polymeric binder which, along with catalyst particles 46, is distributed throughout the thickness of the mat. In preferred example of an electrode 40, porous material 42 is carbon cloth and a matrix of carbon particles and a polymeric binder which, along with catalyst particles 46, is distributed throughout the thickness of the carbon cloth.

FIG. 3 shows an electrode 50 comprising porous electrically conductive material 52. The electrode 50 has oppositely facing major planar surfaces 50a, 50b. In a direct methanol solid polymer fuel cell, electrode surface 50b is adjacent the membrane electrolyte. Catalyst particles 56, effective for promoting the oxidation of methanol, are concentrated at electrode surface 50a. Sufficient catalyst is provided so that substantially all of the methanol, which is introduced in a fluid to the electrode 50 at surface 50a, is oxidized upon



contacting surface 50b. In an example of an electrode 50, catalyst particles 56 are applied to and impregnated into surface 50a of a porous electrically conductive material sheet material  
5 such as carbon fiber paper.

FIG. 4 shows an electrode 60 comprising porous electrically conductive material 62. The electrode 60 has oppositely facing major planar surfaces 60a, 60b. In a direct methanol solid polymer fuel cell  
10 electrode, surface 60b is adjacent to the membrane electrolyte. Catalyst particles 66, effective for promoting the oxidation of methanol, are concentrated at electrode surfaces 60a, 60b. Sufficient catalyst is provided so that  
15 substantially all of the methanol, which is introduced in a fluid to electrode 60 at surface 60a is oxidized upon contacting surface 60b. In an example of an electrode 60, catalyst particles 66 are applied to and impregnated into both surfaces  
20 60a, 60b of porous electrically conductive material 62.

FIG. 5 shows a multi-layer electrode 70 comprising two layers of porous electrically conductive sheet material 72, 74. In a direct  
25 methanol solid polymer fuel cell layer 74 is adjacent to the membrane electrolyte. An active layer 78, comprising catalyst particles 76 is interposed between layers 72, 74. The layers 72, 74 provide structural support for the catalyst-  
30 containing layer 78. Sufficient catalyst is provided so that substantially all of the methanol, introduced in a fluid at layer 72 is oxidized upon contacting layer 74.

FIG. 6 shows a multi-layer electrode 80

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comprising four layers of porous electrically  
conductive sheet material 82, 83, 84, 85. The  
electrode 80 has oppositely facing major planar  
surfaces 80a, 80b. In a direct methanol solid  
5 polymer fuel cell electrode, surface 80b is  
disposed adjacent the membrane electrolyte.  
Catalyst particles 86 are disposed at both major  
planar surfaces of each layer. Sufficient catalyst  
is provided so that substantially all of the  
10 methanol, which is introduced in a liquid to the  
electrode 80 at surface 80a is oxidized upon  
contacting surface 80b.

FIG. 7 shows a multi-layer electrode 90  
comprising five stacked layers of porous  
15 electrically conductive sheet material 92a, 92b,  
92c, 93a, 93b. The electrode 90 has oppositely  
facing major planar surfaces 90a, 90b. In a direct  
methanol solid polymer fuel cell electrode, surface  
90b is disposed adjacent the membrane electrolyte.  
20 Catalyst particles 96 are disposed in layers 92a,  
92b and 92c. Sufficient catalyst is provided so  
that substantially all of the methanol, which is  
introduced in a fluid to the electrode 90 at  
surface 90a is oxidized upon contacting surface  
25 90b. In an example of an electrode 90 structured  
to facilitate escape of gaseous carbon dioxide  
product, porous layers 92a, 92b, 92c are carbon  
cloth filled with a matrix of carbon particles and  
a polymeric binder, and catalyst particles 96 are  
30 distributed throughout the thickness of the layers  
92a, 92b, 92c. Porous layers 93a and 93b are  
carbon cloth which is not filled with a matrix and  
catalyst particles, and are therefore more porous.

FIG. 8 shows a multi-layer electrode 100

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structured to facilitate escape of gaseous carbon dioxide product. Electrode 100 comprises three stacked layers of porous electrically conductive sheet material 102, 103, 104, and has oppositely facing major planar surfaces 100a, 100b. In a direct methanol solid polymer fuel cell electrode, surface 100b is disposed adjacent the membrane electrolyte. Catalyst particles 106 are disposed in layers 102 and 104. Sufficient catalyst is provided so that substantially all of the methanol, which is introduced in a fluid to electrode 100 at surface 100a is oxidized upon contacting surface 100b. Layer 103 has channels 103a formed in its major planar surfaces to facilitate gas transport. In an example of an electrode 100, porous material 102 and 104 is carbon cloth filled with a matrix of carbon particles and a polymeric binder, and catalyst particles 106 are distributed throughout the thickness of layers 102, 104. Layer 103 is carbon fiber paper with channels 103a formed in the surfaces thereof.

Additional materials, such as hydrophobic or hydrophillic polymers, and particulate fillers, may optionally be incorporated into the electrode, for example, to control gas and liquid transport in the electrode.

In the direct methanol solid polymer fuel cells described herein, protons are generated by oxidation of methanol at catalyst sites which are remote from the anode-membrane interface. A mechanism is provided for transporting protons from the catalyst sites to the membrane electrolyte. In preferred embodiments, the anode further comprises proton conductive material which provides a path

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for transport of protons from the catalyst sites to the membrane electrolyte. For example, proton conductive material may be impregnated into the at least one porous layer of the anode or may be applied in a mixture with the catalyst. The proton conductive material may, for example, be an ionomer such as a sulfonated fluoroionomer, for example Nafion. Alternatively, or in addition, the methanol may be supplied to the anode in aqueous acidic solution, the aqueous acid thereby providing a path for transport of protons from the catalyst sites to the membrane electrolyte. Suitable acids include sulfuric acid and perchloric acid.

Any catalyst which is effective for the oxidation of methanol may be employed in the anode of a direct methanol fuel cell. For example, the catalyst can be a metal black such as platinum, a mixture of metals, an alloy, a catalyst mixed with additives to promote electrocatalytic activity and/or inhibit catalyst poisoning, or a supported catalyst such as, for example, a noble metal on a carbon support.

#### Example 1

##### Comparison of Methanol Utilization

#### 25 (a) Preparation of a Conventional Anode

A single layer of carbon supported platinum ruthenium catalyst (Pt/Ru/C: 20/10/70%) was applied to one surface of a sheet of carbon fiber paper (14 x 14 cm, thickness 0.27 mm, Grade CFP090) to give a platinum loading of 1.80 mg/cm<sup>2</sup>.

#### (b) Preparation of a Multi-layer Anode

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Carbon supported platinum ruthenium catalyst (Pt/Ru/C: 20/10/70%) was applied to both surfaces of three sheets of carbon fiber paper (14 x 14 cm, thickness 0.10 mm, Grade CFP030), and the sheets  
5 were stacked together to give a multi-layer anode with the same total platinum loading as in Example 1(a) above, that is 1.80 mg/cm<sup>2</sup>.

Each of the above anodes was tested in a liquid feed direct methanol fuel cell employing  
10 Nafion 117 as the ion-exchange membrane (electrolyte) and a platinum black cathode (4 mg/cm<sup>2</sup> platinum loading). In both cases the fuel cell was supplied with a fixed amount of fuel which was recirculated past the anode. The fixed amount of  
15 fuel was 250 mL of aqueous 2M methanol solution with a 0.5M sulfuric acid concentration, and the operating conditions were as follows:

current density - constant at 200 mA/cm<sup>2</sup>  
temperature = 115°C  
20 air inlet pressure = 35 psig  
air stoichiometry = 3

FIG. 9 is a plot of cell voltage versus methanol utilization for a fuel cell with a conventional (plot A) and multi-layer anode (plot  
25 B) prepared as described in Example 1. The quantity of electricity which would be produced if all of the methanol were used (with complete oxidation) can be calculated. The ratio of the observed output (current x time) to the theoretical  
30 output of the fuel cell is expressed as a percentage methanol utilization in FIG. 9. For the conventional anode, the cell voltage drops sharply when the utilization approaches 60%. This

indicates an inadequate concentration of methanol at the electrode. For the multi-layer anode the voltage drop occurs closer to 80% utilization. The primary reason for fuel utilization loss (that is, the fuel cell producing less current than is theoretically possible) is methanol diffusion to the cathode. Additional contributions to the loss may be due to incomplete oxidation of methanol - less than its electrochemical equivalent of six electrons per methanol molecule. The results indicate that the multi-layer anode improves fuel utilization and reduces methanol diffusion to the cathode.

As used herein the term "substantially completely reacted" indicates that the amount of reactant remaining unreacted is insufficient to detrimentally affect fuel cell performance.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings. It is therefore contemplated by the appended claims to cover such modifications as incorporate those features which come within the spirit and scope of the invention.

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What is claimed is:

1. An electrochemical fuel cell comprising:
  - (a) a first electrode, said first electrode having first and second oppositely facing major surfaces, said first electrode comprising at least one layer of porous material and a sufficient quantity of catalyst disposed within the volume of said electrode between said major surfaces so that a reactant in a fluid introduced to said first major surface of said first electrode is substantially completely reacted upon contacting said second major surface of said first electrode;
  - (b) a second electrode;
  - (c) an electrolyte interposed between said second major surface of said first electrode and said second electrode.
2. The electrochemical fuel cell of claim 1 wherein said first and second oppositely facing major surfaces of said first electrode are planar.
3. The electrochemical fuel cell of claim 1 wherein said quantity of catalyst is distributed substantially uniformly within the volume between said first and second oppositely facing major surfaces of said first electrode.
4. The electrochemical fuel cell of claim 1 wherein said at least one layer of porous material comprises a plurality of stacked layers.

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5. The electrochemical fuel cell of claim 1 wherein said at least one layer of porous material comprises carbon particles.

5 6. The electrochemical fuel cell of claim 1 wherein said electrolyte comprises an ion-exchange membrane.

7. The electrochemical fuel cell of claim 6 wherein said at least one layer of porous material is electrically conductive.

10 8. The electrochemical fuel cell of claim 7 wherein said at least one layer of porous material comprises a proton conductor.

15 9. The electrochemical fuel cell of claim 8 wherein said at least one layer of porous electrically conductive material comprises carbon fiber paper.

20 10. The electrochemical fuel cell of claim 8 wherein said at least one layer of porous electrically conductive material comprises carbon cloth.

11. The electrochemical fuel cell of claim 8 wherein said at least one layer of porous electrically conductive material comprises carbon particles and polymeric binder.

25 12. The electrochemical fuel cell of claim 8 wherein said fluid is a gas.



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13. The electrochemical fuel cell of claim 8 wherein said fluid is a liquid.

14. The electrochemical fuel cell of claim 13 wherein said first electrode is an anode and said  
5 reactant comprises an alcohol.

15. The electrochemical fuel cell of claim 14 wherein said alcohol is methanol and said quantity of catalyst promotes the oxidation of methanol.

16. The electrochemical fuel cell of claim 15  
10 wherein said liquid comprises water.

17. The electrochemical fuel cell of claim 16 wherein said liquid further comprises acid.

18. The electrochemical fuel cell of claim 17 wherein said at least one layer of porous  
15 electrically conductive material comprises a plurality of carbon fiber paper layers each of said layers having two oppositely facing major surfaces, and wherein said quantity of catalyst is disposed on at least one major surface of each of said  
20 layers.

19. An electrode for an electrochemical fuel cell, said electrode having first and second oppositely facing major surfaces, said electrode comprising:

- 25 (a) at least one layer of porous material;  
(b) a sufficient quantity of catalyst disposed within the volume of said electrode between said major surfaces so

that a reactant in a fluid introduced to  
said first major surface of said  
electrode is substantially completely  
reacted upon contacting said second major  
5 surface of said electrode.

20. The electrode of claim 19 wherein said  
first and second oppositely facing major surfaces  
of said electrode are planar.

21. The electrode of claim 19 wherein said  
10 quantity of catalyst is distributed substantially  
uniformly within the volume between said first and  
second oppositely facing major surfaces of said  
electrode.

22. The electrode of claim 19 wherein said at  
15 least one layer of porous material comprises a  
plurality of stacked layers.

23. The electrode of claim 19 wherein said at  
least one layer of porous material comprises carbon  
particles.

20 24. The electrode of claim 19 wherein said  
electrolyte comprises an ion-exchange membrane.

25. The electrode of claim 24 wherein said at  
least one layer of porous material is electrically  
conductive.

25 26. The electrode of claim 25 wherein said at  
least one layer of porous material comprises a  
proton conductor.

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27. The electrode of claim 26 wherein said at least one layer of porous electrically conductive material comprises carbon fiber paper.

5 28. The electrode of claim 26 wherein said at least one layer of porous electrically conductive material comprises carbon cloth.

10 29. The electrode of claim 26 wherein said at least one layer of porous electrically conductive material comprises carbon particles and polymeric binder.

30. The electrode of claim 26 wherein said fluid is a gas.

31. The electrode of claim 26 wherein said fluid is a liquid.

15 32. The electrode of claim 31 wherein said electrode is an anode and said reactant comprises an alcohol.

20 33. The electrode of claim 32 wherein said alcohol is methanol and said quantity of catalyst promotes the oxidation of methanol.

34. The electrode of claim 33 wherein said liquid comprises water.

35. The electrode of claim 34 wherein said liquid further comprises acid.

25 36. The electrode of claim 35 wherein said at

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least one layer of porous electrically conductive material comprises a plurality of carbon fiber paper layers each of said layers having two oppositely facing major surfaces, and wherein said quantity of catalyst is disposed on at least one major surface of each of said layers.

37. A method of reducing reactant crossover from a first electrode of an electrochemical fuel cell to a second electrode thereof, said first electrode having first and second oppositely facing major surfaces, said reactant introduced in a fluid at said first major surface, said first electrode comprising at least one layer of porous material and a catalyst, said fuel cell further comprising an electrolyte interposed between said second major surface of said first electrode and said second electrode, the method comprising:

disposing a sufficient quantity of said catalyst within the volume of said first electrode between said major surfaces such that said reactant is substantially completely reacted upon contacting said second major surface.

38. The method of claim 37 wherein said first and second oppositely facing major surfaces of said first electrode are planar.

39. The method of claim 37 wherein said quantity of catalyst is distributed substantially uniformly within said first electrode volume.

40. The method of claim 37 wherein said at

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least one layer of porous material comprises a plurality of stacked layers.

41. The method of claim 37 wherein said at least one layer of porous material comprises carbon particles.

42. The method of claim 37 wherein said electrolyte comprises an ion-exchange membrane.

43. The method of claim 42 wherein said at least one layer of porous material is electrically conductive.

44. The method of claim 43 wherein said at least one layer of porous material comprises a proton conductor.

45. The method of claim 44 wherein said at least one layer of porous electrically conductive material comprises carbon fiber paper.

46. The method of claim 44 wherein said at least one layer of porous electrically conductive material comprises carbon cloth.

47. The method of claim 44 wherein said at least one layer of porous electrically conductive material comprises carbon particles and polymeric binder.

48. The method of claim 44 wherein said fluid is a gas.

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49. The method of claim 44 wherein said fluid is a liquid.

50. The method of claim 49 wherein said electrode is an anode and said reactant comprises an alcohol.

51. The method of claim 50 wherein said alcohol is methanol and said quantity of catalyst promotes the oxidation of methanol.

52. The method of claim 51 wherein said liquid comprises water.

53. The method of claim 52 wherein said liquid further comprises acid.

54. The method of claim 53 wherein said at least one layer of porous electrically conductive material comprises a plurality of carbon fiber paper layers each of said layers having two oppositely facing major surfaces, and wherein said quantity of catalyst is disposed on at least one major surface of each of said layers.

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FIG. 1A

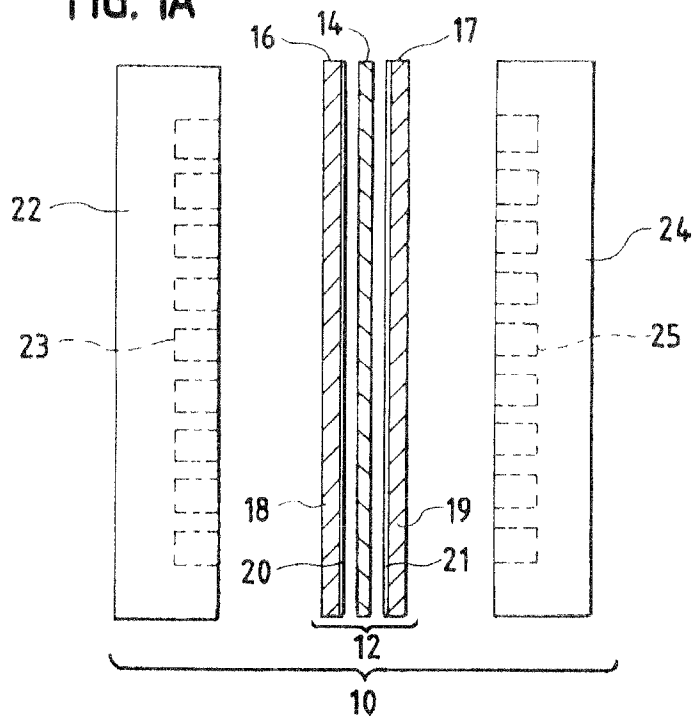


FIG. 1B

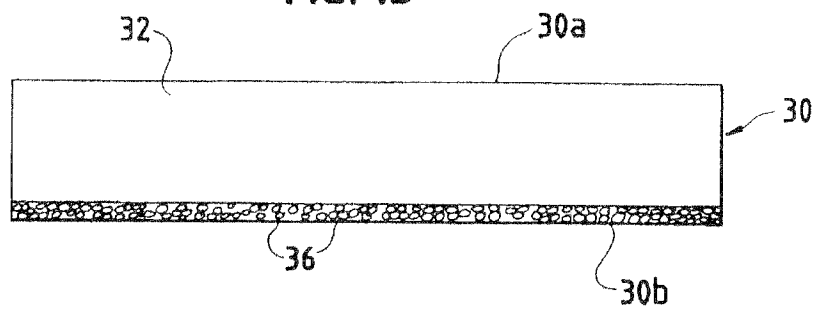
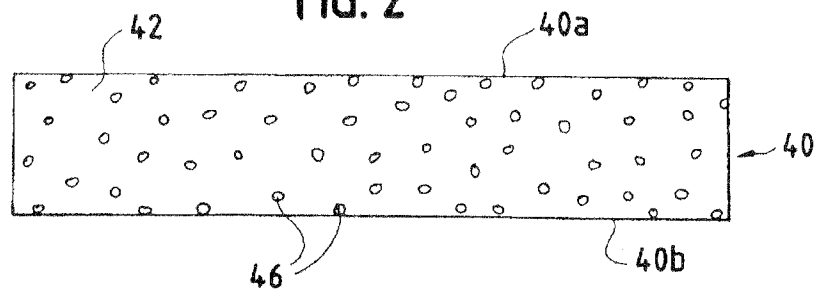


FIG. 2



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FIG. 3

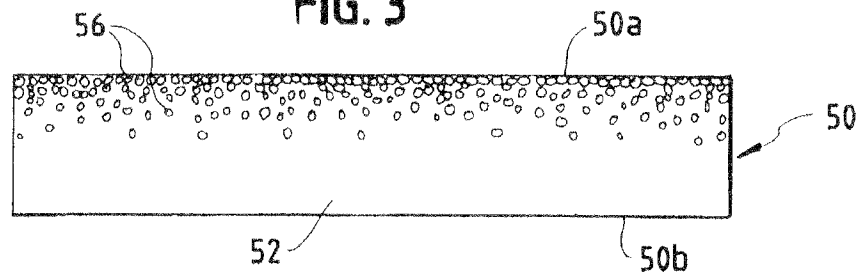


FIG. 4

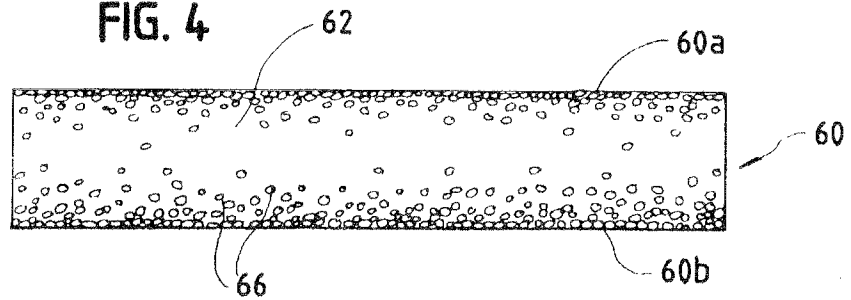


FIG. 5

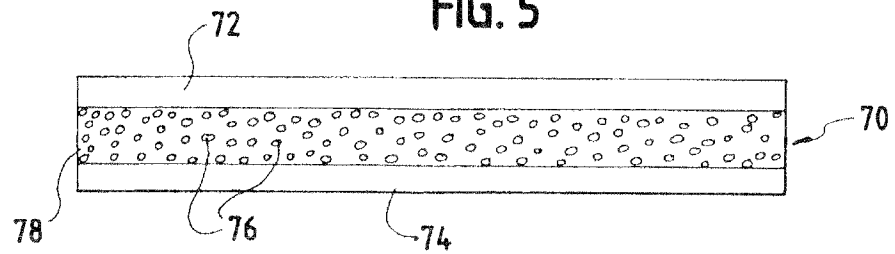
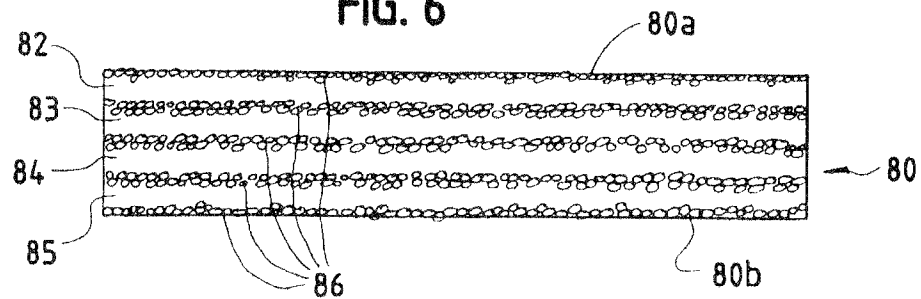


FIG. 6





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FIG. 7

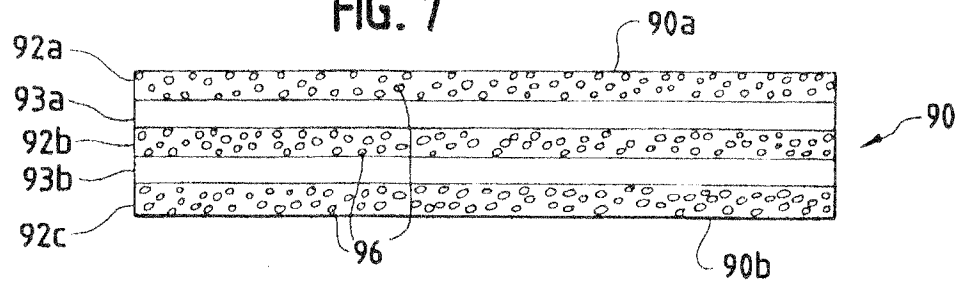


FIG. 8

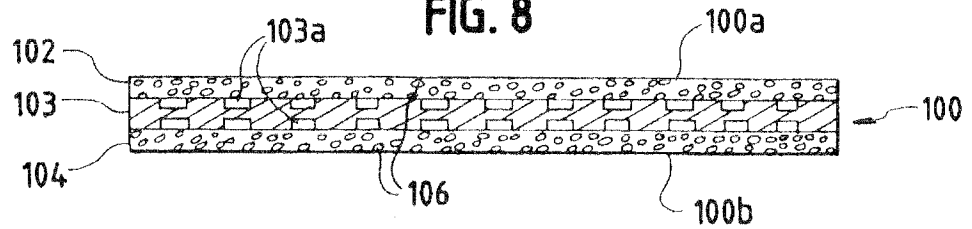
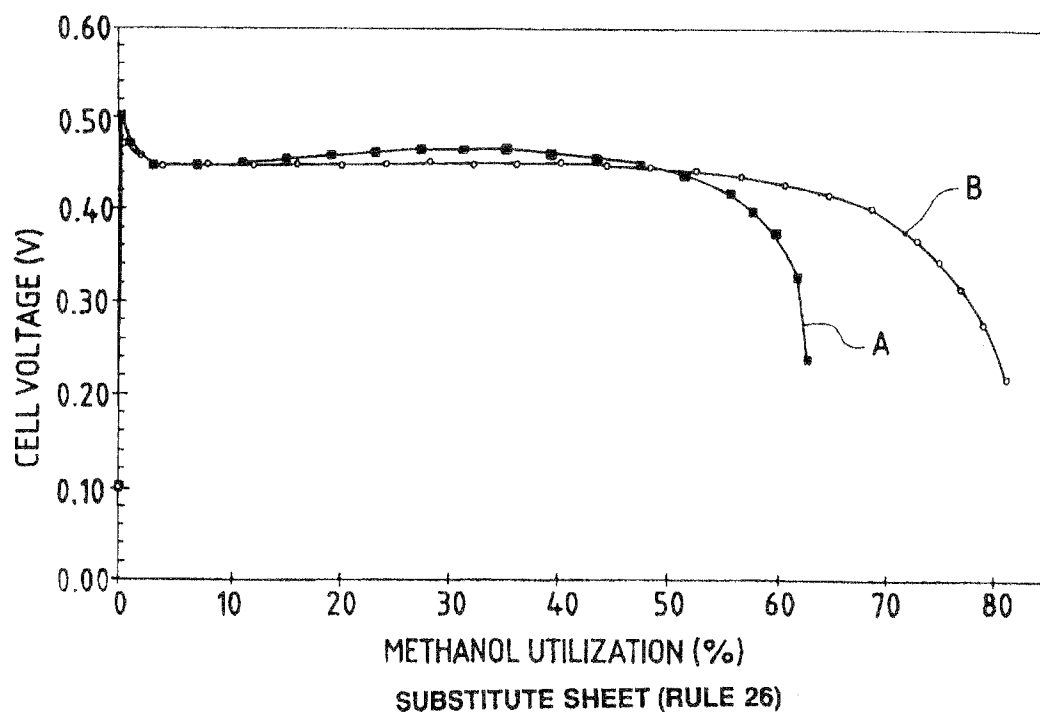


FIG. 9



# INTERNATIONAL SEARCH REPORT

National Application No

PCT/CA 96/00773

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01M4/86 H01M8/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 551 (E-1619), 20 October 1994 & JP 06 203852 A (SANYO ELECTRIC CO LTD), 22 July 1994,	1-3,5-8, 11, 19-21, 23-26, 29, 37-39, 41-44,47
Y	see abstract	4,9,10, 12-18, 22,27, 28, 30-36, 40,45, 46,48-54
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

3 February 1997

Date of mailing of the international search report

27. 02. 97

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 96/00773

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	US 5 523 177 A (KOSEK JOHN A ET AL) 4 June 1996 see figures 1,2 see column 4, line 30 - column 5, line 4 ---	1-54
P,Y	US 5 573 866 A (VAN DINE LESLIE L ET AL) 12 November 1996 see figure 1 see column 2, line 54-58 see column 4, line 25-42 ---	1-54
A	US 5 409 785 A (NAKANO NOBORU ET AL) 25 April 1995 cited in the application see column 4, line 11-40 ---	1-54
A	US 5 132 193 A (REDDY N R K VILAMBI ET AL) 21 July 1992 cited in the application see column 3, line 22 - column 4, line 31 ---	1-54
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 3993248, TICIANELLI E A ET AL: "Dependence of performance of solid polymer electrolyte fuel cells with low platinum loading on morphologic characteristics of the electrodes" XP002024371 see abstract & JOURNAL OF APPLIED ELECTROCHEMISTRY, JULY 1991, UK, vol. 21, no. 7, ISSN 0021-891X, pages 597-605, ---	1-54
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 4610386, SURAMPUDI S ET AL: "Advances in direct oxidation methanol fuel cells" XP002024372 cited in the application see abstract & FOURTH SPACE ELECTROCHEMICAL RESEARCH AND TECHNOLOGY CONFERENCE, CLEVELAND, OH, USA, 14-15 APRIL 1993, vol. 47, no. 3, ISSN 0378-7753, JOURNAL OF POWER SOURCES, 15 JAN. 1994, SWITZERLAND, pages 377-385, -----	1-54

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 96/00773

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5523177	04-06-96	NONE	
US-A-5573866	12-11-96	NONE	
US-A-5409785	25-04-95	JP-A- 5174856	13-07-93
		CA-A- 2085549	26-06-93
		DE-A- 4243600	01-07-93
		JP-A- 6076838	18-03-94
US-A-5132193	21-07-92	AU-A- 8547391	02-03-92
		WO-A- 9202965	20-02-92